

Electronic Supplementary Information ESI for:

Optimizing Optical Properties of Hybrid Core/Shell Perovskite Nanocrystals

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Materials. MA-acetate, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, OA, ODE, OAmBr, PbBr_2 and Cs_2CO_3 were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All reagents and solvents were used without further purification.

Synthesis of MAPbBr_3 Nanocrystals. MA-acetate (136.7 mg, 1.5 mmol), $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (151.8 mg, 0.4 mmol), dried OA (4 mL), and dried ODE (16 mL) were loaded into a 50 mL 3-neck flask and dried under vacuum for 30 min at 50 °C. The mixture was heated to 130 °C and OAmBr (418.1 mg, 1.2 mmol) in toluene (4 mL) was injected under N_2 atmosphere. After 10 s, the reaction mixture was cooled by ice-water bath and kept for later use.¹

Synthesis of Core/Shell $\text{MAPbBr}_3/\text{MA}_{1-x}\text{Cs}_x\text{PbBr}_3$ NCs. PbBr_2 (110.1 mg, 0.3 mmol) and Cs_2CO_3 (326 mg, 0.1 mmol) were loaded into a 50 mL 3-neck flask. Then, dried OA (1 mL), dried ODE (5 mL), dried OLA (0.5 mL), and as-synthesized MAPbBr_3 NCs (12 mL) were added. The mixture was heated to 80 °C under N_2 atmosphere for 20 min. Finally, the reaction mixture was cooled by ice-water bath to prevent further growth of core-shell NCs.

Purification. As-prepared crude solutions of MAPbBr_3 and core/shell $\text{MAPbBr}_3/\text{MA}_{1-x}\text{Cs}_x\text{PbBr}_3$ NCs were put into centrifuge tubes and a certain volume of methyl acetate was added (the volume ratio of crude solution to ethyl acetate is 1: 1), and were then centrifuged at 7000 rpm for 5 min. After that, the precipitate was redissolved in *n*-hexane and centrifuged for 5 min at 5000 rpm. Finally, the supernatant was collected and stored at 4 °C.

Characterization Methods. The size and shape distribution of the NCs were recorded

using an HR-TEM (JEPL, JEM-2100F) at 200 kV. XRD patterns were recorded on a Bruker D8 Advance diffractometer with Cu K α radiation ranging from 10° to 55° at a scanning rate of 4 min⁻¹. UV-visible absorption spectra were recorded on an ultraviolet and visible spectrophotometer (Lambda 950). PL spectrum, absolute PLQY, PL lifetime, and temperature-dependent PL spectrum were collected on an Edinburgh FS5.

Z-scan Measurements. The detailed principle was described in the previous reference.² The fs pulses in the wavelength range of 780-880 nm were output from the OPA system. During the measurements, the fs pulses were focused onto a 1-mm-thick quartz cuvette filled with NC solutions by a spherical lens (focus length: approximately 50 cm). The transmitted light and reference light were measured by two silicon detectors, respectively.

Measurements of Two-Photon-Excited PL and ASE Spectra. A continuously variable neutral density filter was employed to control the incident energy of the pulses. During the measurement of ASE spectra, the laser beam was focused vertically onto the solid film via a cylindrical lens with a focal length of 10 cm, yielding an approximately 0.1 × 5 mm² excitation spot. The two-photon excited PL and ASE spectra from the edge of the solid film serving as the optical waveguide were vertically collected with a compact spectrometer (Ocean optics, HR4000).

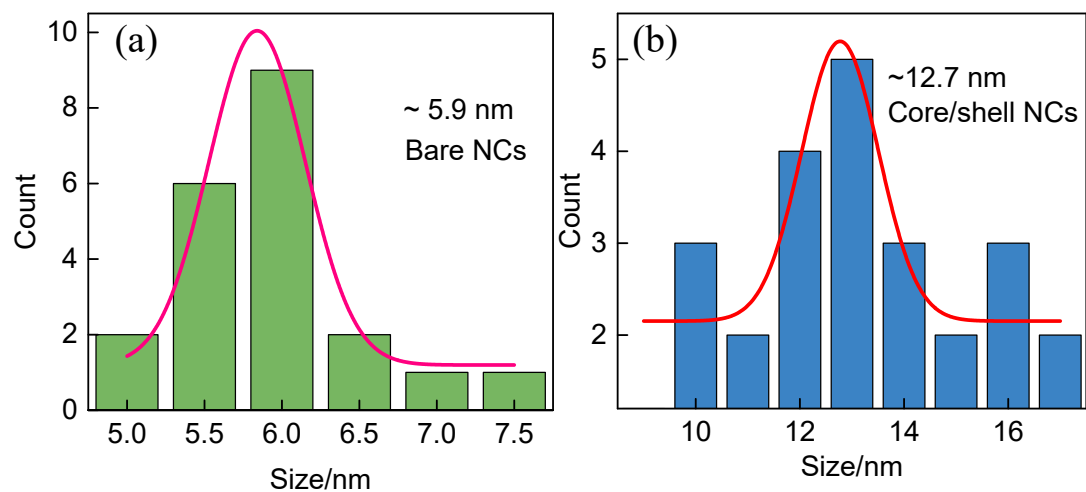


Fig. S1 Size distributions of (a) MAPbBr₃ NCs and (b) MAPbBr₃/MA_{1-x}Cs_xPbBr₃ NCs.

Table S1. Decay components extracted from Fig. 2b

NCs	t_1 (ns)	t_2 (ns)	A_1 (%)	A_2 (%)	t_{ave} (ns)
Bare	13.8	43.7	32	68	25.9
Core/shell	5.8	20.7	24	76	12.9

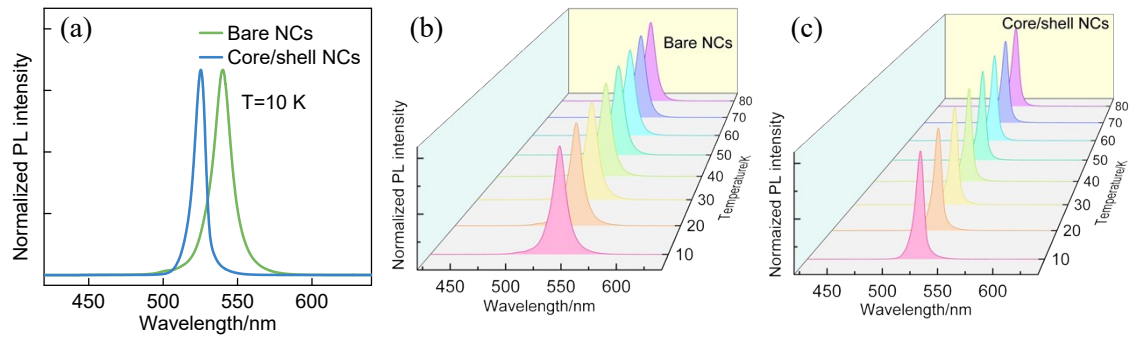


Fig. S2 (a) PL spectrum from the bare and core/shell NCs at 10 K. The normalized PL spectra of (b) bare NCs and (c) core/shell NCs at 10 K-80 K.

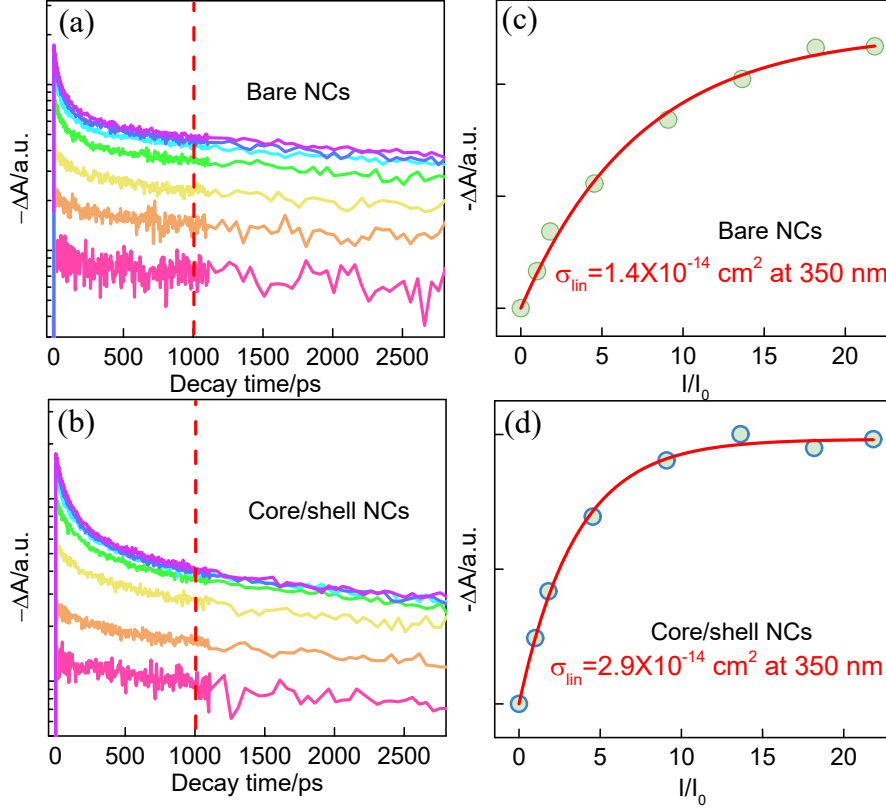


Fig. S3 Excitation intensity-dependent decay traces of (a) bare and (b) core/shell NCs.

The solid curves are best fitting results for (c) bare, and (d) core/shell NCs.

The linear absorption cross-sections (σ_{lin}) of the perovskite NCs at 350 nm were determined through the measurements of the excitation dependent GSB signals at a delay time of 1 ns using fs-TA spectroscopy. The values of σ_{lin} can be obtained from the theoretical fitting based on following equation:^[3]

$$-A\left(\frac{I}{I_0}\right) = -A_{max} \left[1 - e^{-\left(\frac{I}{I_0}\right)\sigma_{lin}I_0} \right], \quad (1)$$

where $A(I/I_0)$ denotes the GSB signal amplitude of NCs after a 1ns delay as a function of excitation intensity, and I_0 is the minimum excitation intensity used in the fs-TA spectrum.

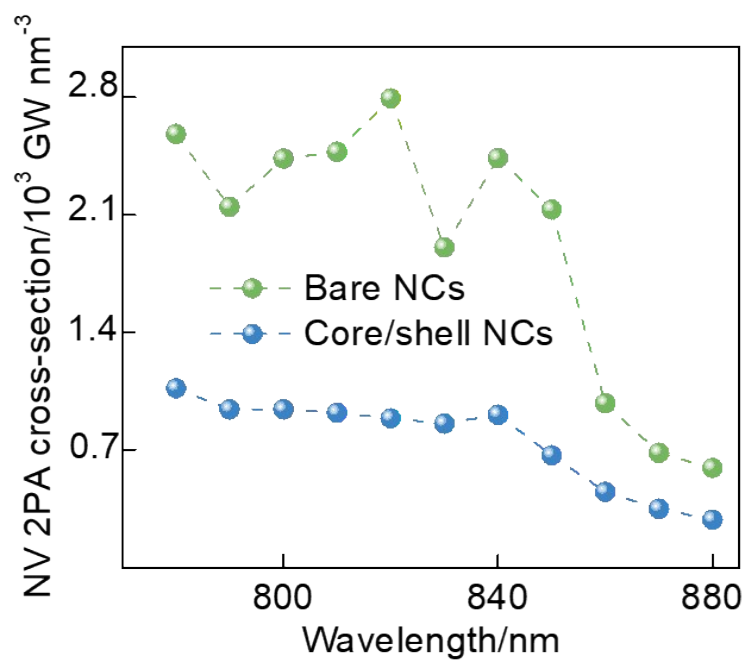


Fig. S4 The volume-normalized (VN) 2PA cross-sections of bare NCs and core/shell NCs.

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